Charging gold nanoparticles in ZnO by electric fields

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Abstract. Controlling the plasmon resonance frequency of metal nanostructures holds promise for both fundamental and applied research in optics. The plasmon resonance frequency depends on the number of free electrons in the metal. By adding or removing electrons to a metal nano-object, the plasmon resonance frequency shifts. In this study we indirectly change the number of free electrons in gold nanoparticles by applying an electrical potential difference over a heterostructure consisting of a ZnO layer with embedded gold nanoparticles. The potential difference induces shifts of defect energy levels in the ZnO by the electric field. This results in an exchange of electrons between particles and matrix which in turn modifies the gold nanoparticle plasmon properties. The positive charge shifts the ZnO optical absorption peak from 377 nm to 386 nm and shifts the nanoparticle plasmon from 549 nm to 542 nm. This electro-optical effect is a promising way to obtain fast optical switching in a solid state composition.

1. Introduction

Optical devices that contain plasmon resonances are of great importance for future high density optical data storage and high-speed signal processing [1]. Plasmonic metal nanostructures have been explored to enhance the performance of solar cells [2-4], increase the sensitivity of detectors [5-6] and energy-conversion devices and sensors [7], stimulate catalysts [8], etc. Besides the applied interest in plasmonics, much research to the fundamentals of plasmonics is performed [9]. For all these topics, controlling the plasmon resonance energy is a very attractive prospect. The plasmon of a metal nanostructure is affected by the size, structure, and composition of both the metal and its surrounding dielectric medium. Moreover, the coupling between the plasmon resonance of a metal and the quantum size effect of a discrete semiconductor nanoparticle gives rise to new properties: semiconductor quantum dot luminescence enhancement through exciton and plasmon coupling [10]. This has been demonstrated in CdSe/ZnS core/shells on Ag nanoislands [11], CdSe on Au [12], colloidal CdSe/ZnS on nanoperiodic Ag arrays fabricated by electron-beam lithography [13], CdSe on thermal evaporated Au layers [14], and ZnO films embedded with Ag nanoparticles [15]. Instead of these static effects on the plasmon, more dynamic control is desired for many purposes. Work by Toyota et al. [16] shows that the plasmon resonance wavelength of gold nanoparticles can be shifted in an electrochemical cell by applying a voltage. Increasing the electron density, and in effect the Fermi level of the metal nanoparticle, shifts the plasmon resonance wavelength [16-17]. Gold nanoparticles with an increased sensitivity to applied voltage can be achieved by decreasing the particle size [18]. Electron transfer to a metal nanoparticle can also occur when the particle is embedded in a semiconductor with appropriate band gap difference which results in Fermi level equilibration and the formation of a nano-Schottky layer. For example, silver nanoparticles on the surface of ZnO nanorods act as a sink for the electrons; they promote interfacial charge-transfer kinetics between the metal and semiconductor, and improve the separation of photogenerated electron-hole pairs, and thus enhance the photocatalytic activity [19]. Dynamically

controlling the Schottky layer, by manipulation of the semiconductor band gap, opens a way to change the charge density on the metal nanoparticle.

Both the Zeeman effect and the Stark effect alter the band structure and change the band gap of semiconductor nanoparticles, upon applying a magnetic or electric field, respectively. Plasmon-enhanced Stark shifts in Au/CdSe core/shell nanoparticles have been demonstrated by Zhang et al. [12]. Spectral shifting towards lower energy of the exciton of Ag-coated CdS semiconductor quantum dots [20], CdSe/ZnS quantum dots assembled on an Ag nanorod array [21], and the exciton of CdSe/ZnS quantum dots assembled on an Ag island film [11] have been reported. Wang et al. [22] have measured the Stark effect of surrounding molecules via the plasmon resonance of the metallic cores.

In this work we embedded gold nanoparticles in ZnO and applied an electric field over the thin film. ZnO is a semiconductor with a normal band gap of 3.37 eV (368 nm) [23]. It is intrinsically an n-type semiconductor with high electron mobility, high thermal conductivity, wide and direct band gap, and large exciton binding energy (60 meV), making it suitable for a wide range of devices, including transparent thin-film transistors [24], photodetectors [24], and light-emitting diodes [25]. Here the ZnO defect levels [26], having attractive (nonlinear absorption) properties [27-28], likely play an important role and are altered by shifting the energy levels under an electric field. This results in a shift of the ZnO exciton peak towards lower energy. By a shift of the defect level energy close to the conduction band of ZnO, electrons will flow to the gold particle, thereby increasing the electron density on the gold particle. This in turn shifts the plasmon resonance wavelength towards higher energy. The controlled dependence of the optical absorption on voltage in the heterostructures studied in this work may have an impact on the technology of electro-optical switches.

2. Experimental

The samples were made with an ultra-high vacuum cluster deposition apparatus equipped with a laser vaporization source which is described elsewhere [29]. The cluster size distribution was monitored

with time-of-flight (TOF) mass spectrometry and is plotted in figure 1(a) as a function of cluster diameter, hereby assuming a spherical shape of the clusters and using a Wigner-Seitz radius of 0.159 nm for gold. Gold clusters are deposited by a laser vaporization source on ITO supports (Präzisions Glas & Optik GmbH) which have surface resistivity less than 20 Ω/sq. After the nanoparticles are deposited on the ITO layer, a layer of 100 nm of ZnO, and 100 nm of ITO were subsequently deposited by RF sputtering at 200 W and 300W, respectively, in a 5 μbar atmosphere (Kurt Lesker). A cartoon of the entire structure is shown in figure 1(b). Because of the low reactivity of gold and the high reactivity of zinc, an oxide layer on gold is not expected [30].

X-ray diffraction (XRD) of all samples on a PANalytical X'Pert PRO X-ray diffractometer (Cu-Kα radiation) showed only the (002) reflection of the ZnO wurtzite structure, pointing out the primary crystallographic orientation along the substrate from the (002) plane. By the Scherrer analysis on the XRD pattern measured in grazing incidence, an average ZnO crystallite size of around 12 nm was deduced. The ITO electrodes were connected with wires by silver conductive adhesive (E-Solder 3021, Epoxy Produkte). A voltage was applied by a power supply (Thurlby Thundar Instruments, El301). Images of the nanoparticles on a silicon wafer were obtained by atomic force microscopy (AFM - Dimension 3000, Veeco Instruments) and analyzed with the WSxM program [31], see figure 1(c). Silicon wafer was chosen as substrates for AFM for its superior adhesion properties compared to ITO on which the particles are swept away by the tip.

The optical absorption was measured by a double-beam, double-monochromator spectrometer (Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer) with a working wavelength range between 175 and 3300 nm with an accuracy of 0.08 nm in the UV-visible region and 0.3 nm in the NIR region. By use of the double beam spectrometer, the absorption of the control sample (sample without gold clusters) was subtracted from the absorption of the sample of interest. This procedure enabled observing absorption of gold clusters within the ZnO surrounding layer. The experiments were performed at room temperature.

3. Results and discussion

The optical absorption of the thin ZnO layer with gold nanoclusters, sandwiched between two ITO layers, was measured as a function of applied voltage. Since the gold particles are largely covered by ZnO, the ITO substrate is unlikely to have a strong effect on the properties of the gold particles. And because ITO is more conductive than ZnO, the electric field will mainly be present in the ZnO [26, 32-34]. In figure 2, the absorption spectrum of gold nanoparticles embedded in ZnO at 0V clearly shows two peaks. The peak at ~550 nm is identified as the plasmon peak of gold nanoclusters in ZnO. The plasmon resonance wavelength depends both on size and surrounding medium. For particles of about 2 nm the plasmon wavelength peaks at around 500 nm in vacuum [35], while the refractive index of the surrounding ZnO (~2 around the gold plasmon resonance [36-37]) causes a significant redshift to 550 nm. The peak at 377 nm originates from excitonic absorption [38]. This ZnO peak is much stronger in the presence of gold clusters, which is attributed to a possible enhancement of the ZnO UV peak caused by plasmonic local field enhancement [21]. The intensity ratio between the UV and visible emissions of ZnO is a classical measure of the material quality because the visible emission occurs due to point defects [39]. From the low absorption in the visible, the ZnO must have reasonable quality (cf. XRD results discussed above). However, some defects, i.e., oxygen and/or zinc vacancies, are present which will affect the electron mobility and work function.

The evolution of the absorption spectrum as a function of forward bias is shown in the Supplementary Information, figure S1. A voltage of 6 V, taking into account the sample thickness, corresponds to 300 kV/cm. The position of the two main peaks (in energy) as a function of voltage is shown in figure 3. The relation between peak energy position as a function of voltage shows a linear dependence, see fitting curves, both for the gold plasmon peak and for the ZnO exciton absorption. The linear dependence points to the first order Stark effect, which indeed has a linear dependence of ΔE on the electric field and therefore voltage [40]. The data are also compatible with a transition to the second order Stark effect; the optical nonlinearity of similar gold nanoparticles within ZnO surroundings has been

demonstrated [30]. In this configuration the Stark effect may act on the defects which are likely introduced around the gold particles.

The position of the ZnO peak shifts to the red by 9 nm (= 69 meV), while this is not the case for the control sample without gold nanoparticles. It is unlikely that this shift is the result of the Franz-Keldysh effect [41-42] because the electric field is too low and in static electric fields the Franz-Keldysh effect shows a blue shift of the band gap peak [43], being proportional to a 2/3 power law of the electric field [44]. The observed magnitude of the shift is rather large when considering the ZnO film thickness and applied voltage; according to literature 300kV/cm could only induce an increase of the ZnO band gap by 6 meV [45]. Considering a total experimental error of 4 nm on the peak position, such an increase of the wavelength peak position was likely not observable in the control measurement. Since during an optical absorption scan a single wavelength is measured and the gold nanoparticle resonance wavelength is far from the ZnO blue peak, a plasmonically enhanced Stark effect is also unlikely. However, the defects (impurities, dislocations, vacancies) introduced in the ZnO layer [46] by the incorporation of the gold nanoparticles and with energies within the ZnO band gap, are likely shifted in energy by the Stark effect. Since many of the defects are close to the Fermi level, a slight shift of the defect level by the Stark effect may result in the release or capture of an electron, for p- and n-type defects respectively. Since these defect levels are of importance to the optical absorption of ZnO, the excitonic peak is shifted as a function of applied electric field. A redshift can be explained by the increase of a p-type defect level energy (2p-orbital electrons of oxygen ions within ZnO transferred to gold nanoclusters), which leads to the release of an electron (to the gold particle) [24, 47]. The empty defect level below the conduction band then becomes optically active, leading to a redshifted absorption [48-49]. Hence, applying the field results in charge transfer from the ZnO to the gold nanoparticle and the other way around with synergetic effects on both optical properties. Therefore, the redshift of the ZnO peak at 377 nm (3.29 eV) can be explained by the activation of defects with respect to optical transitions through electron release [50-51].

The measured electric currents through the device (up to 300 mA) could lead to an increase of the device temperature with several hundreds of degrees. Since the optical properties of ZnO depend on the

temperature [52] a release of electrons from the p-type defects could also be caused by the higher temperature as a result of the current flow.

The effect of the electric potential on the gold Fermi level was investigated by reversing the potential polarity. Because the gold particles are only located at one side of the sample, this asymmetry should result in an opposite Fermi level shift upon polarity change. This would translate into either blue shifted or redshifted gold plasmon resonance peaks, which was not observed. Therefore, instead of the effect of potential, it is the electric field which affects the optical response which is schematically illustrated in figure 4. The independence of the optical response on the polarity also makes chemical reactions, induced by the electric field or potential, unlikely since such reactions are sensitive to the voltage sign.

The position of the gold plasmon peak shifts to the blue by 7 nm or 29 meV (which is a 1.3 % shift of its original value) at the maximum applied voltage. Because of the different work function between a metal and semiconductor, charge transfer occurs already without applied voltage and forms a Schottky layer [53-54]. The work function of gold and ZnO is 5.1 eV [55] and 4.45 eV [56], respectively. This difference in work function results in electron transfer from ZnO to the gold clusters. This mechanism is schematically illustrated in figure 4.

Since the electron density on the metal particle determines its plasmon resonance energy [16-17, 57] $\omega^2_p = Ne^2/m\varepsilon_o$, with N=electron density, e=electron charge, m=effective electron mass and ε_o=vacuum permittivity, this charge transfer will change the gold cluster plasmon resonance wavelength. Extrapolating the measurements of Toyota et al. [58] a blue shift of 1.8 nm per electron is estimated for a 2.3 nm gold nanoparticle. Therefore, the shift of 7 nm observed here at maximum applied voltage corresponds to 3.8 electrons per particle on average. The change of the defect energy by about 69 meV is responsible for the transfer of these electrons. According to Zhdanov [59], the electron density on a small metal particle embedded in a semiconductor is much smaller as compared with a metal layer in a conventional Schottky layer because the charge is only located at the surface of the metal nanoparticle. The transfer of 3.8 electrons is realistic when compared with this Zhdanov theory, where about 4.8

electrons would move from ZnO to the gold particle. The number of transferred electrons as a function of potential is shown in figure S2, and is in good agreement with literature values.

Note that the absorbance of the gold clusters is about 3 times smaller as compared to the ZnO peak, see figure 2. Both peaks also increase in magnitude with increasing voltage and the absorbance intensity change of the ZnO peak is about twice larger than for the plasmon peak. Because the plasmon resonance frequency shifts away from the interband transitions, it increases the oscillator strength [60-61]. This in turn will increase the absorption cross section and the plasmonic strength, explaining the increase in absorption.

An alternative explanation could be found in the dependence of the refractive index on the electric field. Although not much literature is available, Nagata et al. [62] show that the refractive index of a doped ZnO film does not change under an applied electric field. The decrease of the plasmon absorption intensity could be caused by the shift of the plasmon resonance closer to the interband transitions. In a wet electrochemical experiment it was proposed that plasmon dampening by the presence of adsorbates on gold nanoparticles is causing the shifts [63]. In our case with gold clusters embedded in a stable ZnO matrix, it is unlikely that surface effects are responsible.

4. Conclusions

By applying an electric field over a ZnO layer with embedded gold clusters, electrons flow from ZnO to the gold particles whereby the electron density on the embedded gold clusters is changed. This may be caused by the Stark effect or elevated tempratures acting on defect energy levels. The change in electron density by just 3.8 electrons per particle on average shifts the gold particle plasmon resonance wavelength by about 7 nm. The positive charge in the ZnO matrix shifts its optical absorption peak at 377 nm to lower energy. The interdependent change of both exciton and plasmon wavelength of a heterostructure based on a metal-semiconductor contact provides a controlled way of electrical charging

of metal nanoparticles. This study represents a promising method to investigate the plasmon properties of metal nanoparticles which for example exhibit quantum effects. Changing the strength of the optical interaction with the metal nanoparticle and shifting the plasmon resonance wavelength are interesting for a wide range of optical devices such as electro-optical switches for telecommunication.

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Figures

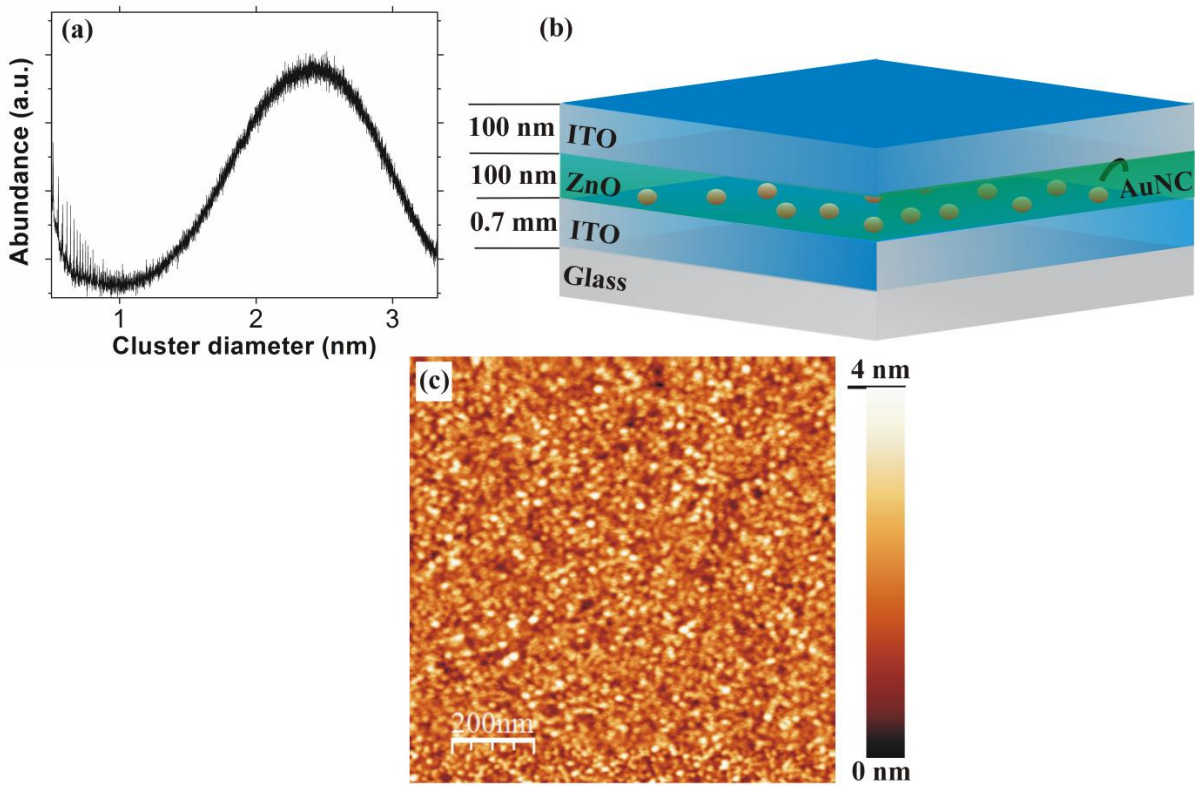

Figure 1. (a) Gold cluster size distribution as measured by a time-of-flight mass spectrometer. The cluster diameter is deduced assuming a spherical cluster shape and a gold Wigner-Seitz radius of 0.159 nm. (b) Schematic diagram depicting the sample. (c) AFM image of gold clusters deposited simultaneously on a Si wafer.

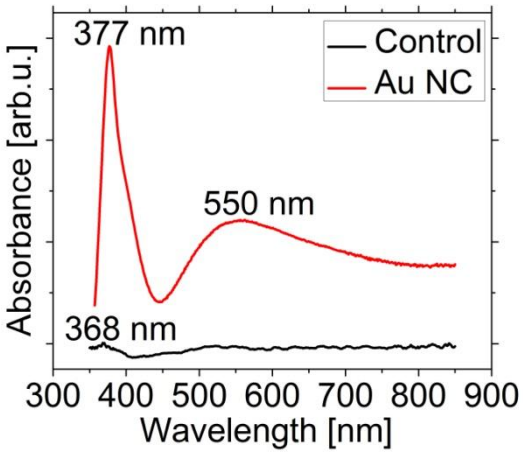

Figure 2. Absorbance spectrum of a thin ZnO layer of a control sample without clusters (black) and of a thin ZnO layer with gold clusters (red) at 0 V.

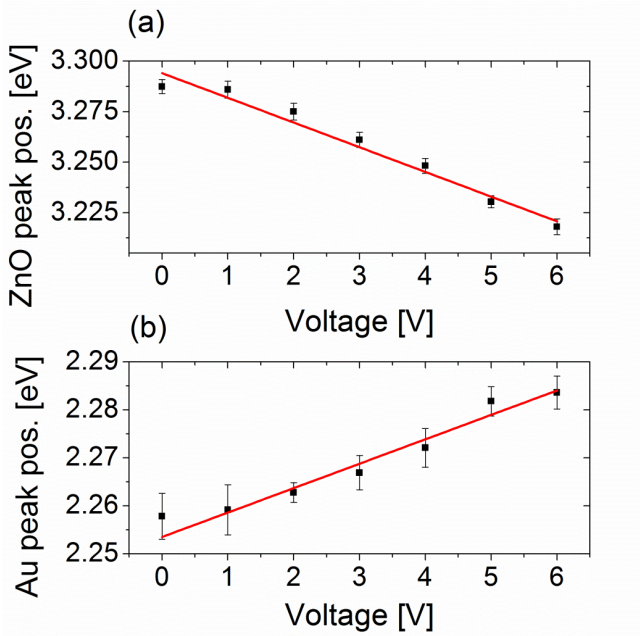

Figure 3. The energy position of (a) the ZnO peak at 3.29 eV (377.2 nm) and (b) the gold peak at 2.26 eV (549.2 nm) as a function of applied voltage. The red curves in both plots are the linear fitting of the measured data.

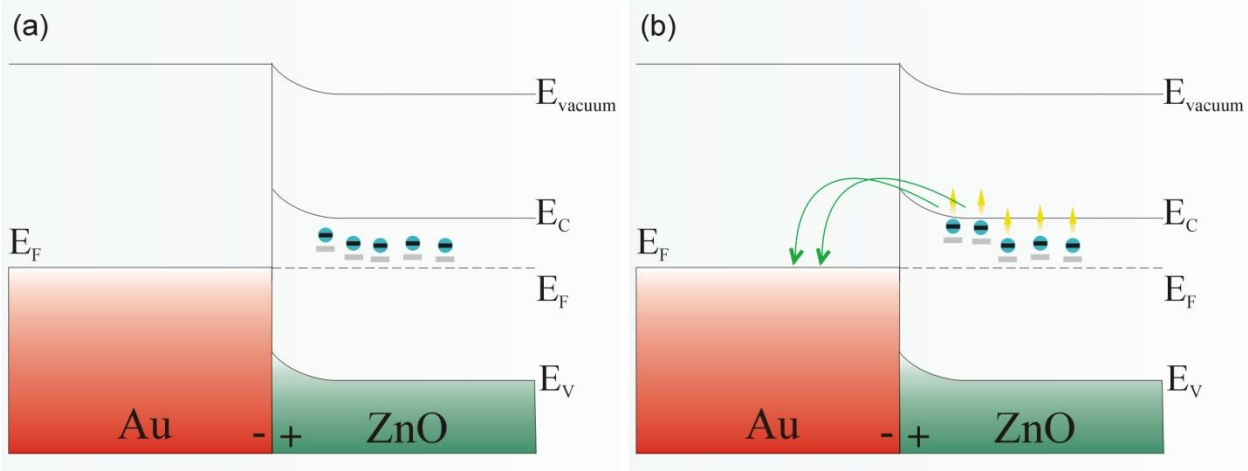

Figure 4. Schematic drawing illustrating the proposed mechanism. (a) The difference in work function between the nanoclusters and the matrix leads to electron transfer from the conduction band of ZnO to the conduction band of gold. (b) Upon applying a voltage via electric field (represented by the vertical yellow arrows) the p-type defect levels shift which results in electron release into the gold particle. As a consequence the observed optical absorption will be shifted.

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